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Production of Hydrogen Bromide by Bromine-Methane Reactions at Elevated Temperature

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ABSTRACT

Hydrogen bromide is a potentially useful intermediate for hydrogen production by electrolysis because it has a low cell potential and is extremely soluble in water. Processes have been proposed to exploit these properties, but among the important issues to be resolved is the efficiency of HBr production from hydrocarbon precursors. This investigation evaluated a fundamental facet of such a technology by studying the reaction of methane and bromine at elevated temperature to determine the yield and kinetics of HBr formation. Laboratory experimentation and computational chemistry were combined to provide a description of this reaction for possible application to reactor design at a larger scale. Experimental studies with a tubular flow reactor were used to survey a range of reactant ratios and reactor residence times at temperatures between 500°C and 800°C. At temperatures near 800°C with excess methane, conversions of bromine to HBr exceeded 90% and reaction products included solid carbon (soot) in stoichiometric amounts. At lower temperatures, HBr conversion was significantly reduced, the products included much less soot, and the formation of bromocarbon compounds was indicated qualitatively. Calculations of chemical equilibrium behavior and reaction kinetics for the experimental conditions were performed using the Sandia CHEMKIN package. An elementary multistep mechanism for the gas-phase chemistry was used together with a surface mechanism that assumed facile deposition of radical species at the reactor walls. Simulations with the laminar-flow boundary-layer code of the CHEMKIN package gave reasonable agreement with experimental data.

Acknowledgments

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Production of Hydrogen Bromide by Bromine-Methane Reactions at Elevated Temperature

Introduction

A hydrogen production process that requires the formation of hydrogen bromide as one of the primary steps has been proposed by the SRT Group, Inc., Miami, FL. SRT has described the process and preliminary development studies in detail elsewhere, so only the basic features are given here.[1,2] The SRT process is based on forming hydrogen bromide by reacting bromine and a hydrocarbon, e.g., methane. This reaction must be performed at elevated temperature and process design studies anticipate a temperature of 800°C. The HBr generated by the reactor is collected with water to produce concentrated hydrobromic acid that is electrolyzed in a separate process step, yielding hydrogen and bromine. The bromine is recycled to the reactor to perpetuate the HBr production cycle. The hydrogen may be used to generate energy by various means. Alternatively, both constituents may be used to produce electrical power via a regenerative hydrogen-bromine fuel cell.[3]

Sandia National Laboratories (SNL) has participated in the development of the chemical process to produce hydrogen bromide by conducting studies to determine the fundamental behavior of bromine-methane reactions with regard to their yield and kinetics. These studies will provide the technical basis for reactor engineering of the SRT process.[4] The SNL work consists of several tasks. One task is to conduct laboratory experiments to determine the characteristics of the reactions of bromine and methane at elevated temperature that produce hydrogen bromide. This task is coupled with computer modeling of the reactor kinetics in order to determine the underlying chemical mechanism. With a validated mechanism, computation can be used to predict the extent of the desired reaction and the formation of by-products for a wide range of reactor conditions.

This report describes the experimental study and computational chemistry analysis conducted at SNL to determine the rates and conversion of the reaction of bromine and methane at temperatures up to 800°C. Laboratory experiments described in this report provided data that were used to develop the chemical kinetics mechanism, rather than demonstrate the process as it might be used in production. An experimental reactor was designed and constructed to allow a broad envelope of reaction conditions to be evaluated. The variables that define this envelope are the reactor temperature, the ratios of the reactants in the feedstock, and the residence time in the reactor. The extent and rate of the reactions were determined by chemical analysis of both gaseous and condensed products from the reactor effluent. These techniques include both on-line gas chromatography and off-line analysis.

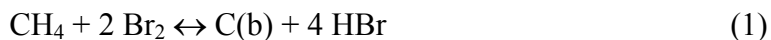
Computational Thermochemistry

This section summarizes the calculations that were carried out to determine the feasibility of producing hydrogen bromide from methane and bromine at elevated temperatures. As is customary in such investigations, the process was first examined from a thermodynamic point of view to determine whether it was viable. Kinetic simulations were then carried out to estimate whether the time scales were reasonable. It must be emphasized that the results presented here are not definitive because the underlying chemical mechanisms are probably incomplete, some of the data are of uncertain accuracy, and a detailed parameter study was not performed. These calculations were intended to be used mainly as a guide for the companion experiments that were subsequently conducted at SNL and are discussed below. Among other things, the calculations enabled the experimental apparatus to be designed with full regard for all of the reaction products that might be formed. Such calculations also provide useful information regarding the energetics of the reactions. The results of the experiments were used to validate the models so that they could later be used with confidence in detailed reactor simulations.

Two primary sources were used to assemble the gas-phase mechanism and data needed for the calculations. The species and reactions involved in methane pyrolysis were taken from GRI-Mech Version 1.2, and the corresponding thermodynamic data file was used as the default. Reactions and thermodynamic data for bromine-containing species were obtained from a NIST Web site [5]. Several reactions tabulated by Babushok [6] but not included in the NIST Web site (perhaps because of uncertain accuracy) were added to our compilation. Sixteen miscellaneous reactions from various sources were also added, partly to provide a pathway for complete bromination of methane. Thermodynamic data for all bromomethanes and bromomethyl radicals were obtained by fitting the values reported by Paddison and Tschuikow-Roux [7] and were used to complement the NIST database. The complete gas-phase mechanism is presented in Table I, which is the output file produced by the CHEMKIN Interpreter [8].

The next step was to perform a purely thermodynamic analysis to determine the relative amounts of the species present in the system at equilibrium. Results were obtained as a function of temperature at a fixed pressure of 1 atm. The computations were carried out using the EQUIL code, which is basically a CHEMKIN interface to the well-known STANJAN code. The results were checked against both a spreadsheet-based calculation at 25°C and the predictions of the online solver EQUILIB-Web [9]. Both STANJAN and EQUILIB-Web have certain advantages: the latter automatically, and almost effortlessly, gives the global equilibrium composition by including every species in its database, while the former allows one to perform partial equilibrium calculations by including only those species that are of interest. We used STANJAN in this case in order to take advantage of its flexibility.

For a system that produces HBr most efficiently from bromine and methane, the overall reaction is



where C(b) is bulk or solid carbon (graphite). This stoichiometry was input to STANJAN, and the results are shown in Figure 1. Note that the ordinate is the *overall* mole fraction, on a logarithmic scale, with both gaseous and solid constituents included. Clearly, the conversion of methane to carbon is essentially complete; the formation of HBr is also nearly complete at low temperatures, but at higher temperatures HBr begins to dissociate into H₂ and Br₂, and eventually Br₂ itself begins to dissociate. Brominated hydrocarbons are not formed in significant amounts under these circumstances.

The rate of formation of solid carbon must depend on the surface-to-volume ratio in the reactor, although the surface may include more than just the reactor walls. Because of this dependence, it is possible that carbon deposition may not actually occur to a significant extent under some conditions of practical interest. Therefore, it is useful to carry out partial equilibrium calculations in which solid carbon has been deleted. Using the same list of gas-phase species as before, one obtains the results shown in Figure 2. Obviously, the situation is now far more complicated. HBr is still the dominant species in the gas, but there is a significant amount of free Br₂, even at relatively low temperatures, and the carbon is distributed among a wide variety of bromocarbons and hydrocarbons. For kinetic simulations in which solid carbon is not included, one might well expect these same gaseous species to appear. However, it must be emphasized that partial equilibrium calculations like these must be interpreted cautiously, because the results are entirely dependent on the list of species that one chooses to include.

In order to determine whether the equilibrium composition just described could actually be achieved, a time-dependent reactor simulation was carried out using the full kinetic mechanism in Table I. Only gas phase species were included in the calculation, because the mechanism for solid carbon deposition is not known with any certainty, and also because heterogeneous chemistry involves surface area and transport issues that depend strongly on the particular reactor configuration. It was recognized that a surface reaction mechanism would have to be added later if experiments showed that carbon was being deposited in significant amounts. Regardless, the preliminary simulation was carried out using the CHEMKIN plug-flow reactor code PLUG. PLUG is a steady-state code, but the residence time in the reactor assumes the role of the actual time in a transient code, and plotting the results as a function of time makes them more generally useful.

The predicted evolution of the mixture composition is shown in Figure 3. Note that both the species concentrations and the residence time are plotted on logarithmic scales in this figure.

The initial temperature is specified as 600°C, but the reactor is taken to be adiabatic, so the temperature varies with time as shown in Figure 4. From Figure 3 it can be concluded that the dominant reaction during the earliest stages of the process is the formation of methyl bromide,



This is quickly followed by the appearance of the other bromomethanes; the bromination sequence is obviously very exothermic and is essentially complete within 0.01 s. The high temperature also leads to significant dissociation of elemental bromine. At longer times, the initial products are replaced to some extent by the unsaturated compounds $\text{C}_2\text{H}_3\text{Br}$ and C_2H_2 , which are formed endothermically. However, it is clear that the process has not reached equilibrium even after 10^4 s, so the final composition does not match that given in Figure 2 for the final temperature of 685°C. In any case, the large concentration of brominated hydrocarbons is a cause for concern, and it will be crucial to determine whether deposition of solid carbon can prevent the formation of these compounds, as suggested by the equilibrium calculations.

Summarizing these computational feasibility studies, the equilibrium conversion of bromine to HBr for a stoichiometric feed stream is excellent, especially at low temperatures. If equilibrium is actually achieved, then the other principal product is solid carbon in some form, e.g., coke or soot. If solid carbon is not produced, then the effluent gas will almost certainly contain significant amounts of brominated hydrocarbons. Not only do these toxic substances present a disposal problem, but they represent a loss of bromine from the system and an incomplete use of the hydrogen introduced in methane.

With regard to kinetics, it appears that the gas phase chemistry takes place on multiple time scales. However, most of the HBr is produced within a small fraction of a second at 900°C. Since the formation of solid carbon can only accelerate the approach to equilibrium, it is safe to conclude that the process is kinetically feasible at reasonable temperatures. Even so, it should be acknowledged that there are several sources of uncertainty in the calculations. First, it is possible that the gas-phase reaction mechanism as it stands is incomplete, in part because it was assembled largely from independently constructed sub-mechanisms for bromocarbon chemistry and methane pyrolysis. In particular, the role of larger and more highly unsaturated bromocarbons could be important. In addition, many of the reactions involving bromocarbons have historically been investigated from the point of view of atmospheric chemistry, so their rates have not been measured at the elevated temperatures of interest in the current process. Arrhenius extrapolation of these rates beyond the range of measurement is somewhat uncertain, but in the present case there is no alternative. For these reasons, the experimental program conducted at SNL has been crucial in providing data for model validation.

Experimental Methods

Reactor apparatus

The basic design chosen for the experimental apparatus was a tubular reactor in which non-reactive gases (nitrogen and argon) were used to sweep relatively dilute amounts of the reactive gases, methane and bromine vapor, through the heated reactor and into the analytical section of the system. The technique of sweeping the reactants, and products, with inert gases facilitated control of the molar ratios of bromine and methane and allowed the residence time to be controlled as well. Dilution of the reactants also simplified the handling of bromine, while still providing an adequate amount of output for chemical analysis. The reactor system was designed primarily to measure the amount of HBr produced and the residual concentration of methane in the effluent.

The reactor assembly is shown schematically in the upper illustration in Figure 5. A photograph of the assembled reactor system is shown in the lower illustration in Figure 5. The elements in the photograph correspond generally to the schematic diagram. The entire reactor apparatus, except for the gas chromatograph, was housed in a walk-in fume hood to contain any hazardous vapors. The furnace was a resistively-heated three-zone unit and had a heated region 10 in. long by 6 in. diameter (Model 3210, Applied Test Systems, Inc., Butler, PA). Power was balanced to each zone to provide temperature uniformity of $\pm 10^{\circ}\text{C}$ over the length of the reactor tubing coils. The furnace was controlled by a thermocouple located in the center, and several other thermocouples were distributed along the reactor to monitor the reactor temperature. Methane and argon were supplied by the compressed gas cylinders shown at lower left in the fume hood and the flow rates were regulated by rotameters (upper left panel). The gases entered the reactor tube (visible within the furnace cavity) on the left side of the furnace and exited on the right. The gases passed through a series of traps and scrubbers to collect the products, e.g., HBr, before the residual permanent gases were analyzed by a gas chromatograph.

Methane was supplied to the reactor as a 10% (volume) mixture in nitrogen. Bromine vapor was supplied by a device that saturated a carrier gas (argon) that was bubbled through liquid bromine. The concentration of bromine in the saturated gas stream was determined by its vapor pressure at the temperature of the liquid. The bromine saturator assembly was immersed in an ice-bath because bromine is a highly volatile liquid. The design of the bromine saturator followed that described by Mock [10] and was fabricated from Pyrex glass. A photo of the saturator is shown in Figure 6. This figure also shows an empty saturator vessel which was located downstream to collect any aspirated bromine droplets produced by the bubbler. The inlet and outlet fittings of the saturator and the collector were Ace-Thred® #7 compression fittings (Ace Glass Co., Vineland, NJ) and were made of PTFE. FEFTE O-rings were used to seal the 0.25 in. O.D. FEP tubing that conveyed the bromine-containing gas stream. The bromine-containing argon stream and the methane-nitrogen mixture were mixed in a manifold at room temperature before entering the reactor.

The reactor tubes were fabricated from quartz (Allen Scientific Glass, Boulder, CO) and were sized to allow a range of residence times to be studied. The reactor tubes were formed as

spirals, resembling condenser coils, so that they would fit within the uniformly-heated region of the furnace. One reactor tube was made with four and one-half turns of tubing having an I.D. of 10 mm and had an effective heated volume of 80 cm³. A larger reactor tube was made with eight turns of tubing having an I.D. of 12 mm and had an effective heated volume of 280 cm³. A photograph of the larger reactor tube mounted in the furnace is shown in Figure 7. The photograph also shows the array of thermocouples used to monitor the temperature of the tube at several locations. The reactor tubes were terminated with quartz spherical joints in order to connect to the inlet and outlet apparatus. These joints were coated with fluorinated stopcock grease (Dupont Krytox GPL205, Ace Glass Co., Vineland, NJ) to provide leak-free sealing compatible with bromine vapor and hydrogen bromide. A number of custom quartz and Pyrex items were fabricated to construct the reactor apparatus, including the bromine saturator stages, inlet gas mixing manifold, a hot effluent quench chamber, liquid traps for reaction products, and numerous adapter pieces. These items were assembled on a supporting latticework in the walk-in hood that housed the reactor and furnace, as shown in Fig. 6. The entire flow path (tubing, valves and fittings) consists of the bromine-compatible materials quartz, Pyrex, and several types of fluorinated polymers, FEP, FETFE, Kalrez and PTFE.

Gas flow rates were measured in the initial experiments using rotameters calibrated by comparison with a NIST-traceable mass flow meter (Model RC3600, Thermo-Orion, Beverly, MA). The reactor typically operated at 2-3 psi above atmospheric pressure due to the back-pressure created by the scrubbers and traps. The gas flow metering apparatus was subsequently upgraded to provide more accurate measurements than can be achieved by rotameters. Mass flow meters for nitrogen and argon (Model 8270, Matheson Gas Products, Montgomeryville, PA) were installed on the feed lines from the gas cylinders and were recalibrated for the gases used in the HBr reactor by comparison with the RC3600 mass flow meter. We were able to obtain better proportioning of the reacting gas flows and to confirm that the rate of supply of bromine from the vaporizing device performed according to its design. As discussed below, this upgrade also allowed us to obtain a quantitative mass balance on carbon by comparing the cumulative inlet flow of the methane-nitrogen mixture to gravimetric measurements of the amount of solid carbon (soot) collected in the reactor tube and an effluent stream filter, loosely packed with glass wool, that was located before the traps and scrubbers.

The gases exiting the reactor were passed through a series of traps to remove HBr quantitatively for chemical analysis as well as to protect the gas chromatograph from possible damage by HBr or bromine. The traps consisted of an ice trap (0°C), a dry ice-isopropanol (IPA) trap (-75°C), and two aqueous scrubbers in series. The aqueous scrubbers were immersed in ice baths to minimize the amount of water vapor in the scrubbed gas stream. The ice trap was intended to collect C-H-Br compounds having relatively high melting and boiling points, for example, carbon tetrabromide (melts at 90°C, boils at 190°C) and bromoform (8°C, 150°C).[11] However, bromine (-8°C, 68°C) would not be collected by the ice trap because the partial pressure did not exceed 40 torr at the inlet to the reactor and was less at the exit. Bromine, methyl bromide (-93°C, 4°C) and dibromomethane (-53°C, 97°C) could be trapped by the dry ice-IPA trap if present in sufficient concentrations. Hydrogen bromide (-86°C, -67°C) would not be collected by either of the cold traps because its partial pressure

would be too low because of dilution by the sweep gases. The aqueous scrubbers collected HBr by dissolution and were analyzed after each run to determine the acidity. Specifically, hydrobromic acid was collected by passing the cold-trapped gas stream through two scrubbers that contained several hundred milliliters of deionized water. Gas dispersion tubes were used to produce small bubbles in the scrubbers and enhance absorption by the water. In practice, it was observed that the acidity of the downstream scrubber was ordinarily 3 pH units higher than that of the first scrubber. The scrubber solutions were stored in sealed polyethylene or FEP-coated polyethylene bottles for subsequent quantitative analysis of HBr by titration as described below.

Operating procedure

The furnace and reactor tube were brought to operating temperature while nitrogen flowed through the reactor tube and traps to flush air admitted during decoking and during replacement and cleaning of filters, traps, scrubbers, etc., from the preceding run. The mixture of gases intended for the test was established, while bypassing the bromine reservoir, and sampled with the GC to ensure that the system was operating as intended. The argon sweep gas was then bubbled through the bromine reservoir and mixed with the methane stream in the inlet manifold. The presence of bromine vapor was readily apparent by its characteristic brown color and the start of the run was taken as the time that bromine vapor first appeared at the inlet side of the furnace. The flow rates, temperatures, reactor pressure, and visible indications of reaction products were monitored for the duration of the experiments, which ranged from 25 min. to 1 hour. Total flow rates ranged from 150 sccm to 350 sccm, depending on the test conditions chosen. In some experiments, the data from the mass flow meters and one of the reactor tube thermocouples were acquired by a Macintosh SE computer (Apple Computer, Cupertino, CA) using WorkBench SE data acquisition software (Omega Engineering, Stamford, CT). A typical plot of this data appears in Figure 8 and demonstrates that constant reactor conditions were maintained. The exiting gas, after scrubbing, was sampled at intervals of about 2 minutes by the GC. After a period of operation sufficient to maintain steady-state conditions in the reactor for the majority of the run and to obtain an adequate amount of materials in the scrubbers and traps, the bromine reservoir was shut off to define the duration of the experiment. The reactor tube was decoked after almost every run by oxidizing the soot deposit with a flowing air stream at a temperature of at least 500°C until the soot was completely removed.

The delivery of bromine to the reactor was measured by weighing the bromine bubbler and the aerosol collector before and after each run. The bubbler and collector were sealed with tared PTFE threaded plugs, allowed to warm to room temperature, and thoroughly wiped to remove the external condensation from the laboratory atmosphere before weighing. Bromine delivery was determined by weight difference and was used to calculate the concentration of bromine in the input gas stream as the flow rates of these streams were also measured. These gravimetric data revealed that the performance of the bromine bubbler was quite consistent from run-to-run. The bubbler operated as if the effective temperature was -1°C, rather than the 0°C of the ice bath, slightly less than complete saturation. Vapor pressure data for bromine were obtained from Ref. 12.

Analytical methods

Analysis of product gas stream

The composition of the gas stream from the reactor was analyzed by gas chromatography (GC) to determine the residual amount of methane. Gas samples were withdrawn automatically about every two minutes during a reactor run. This cycling time was determined by the elution times necessary for the GC analytical methods used. In order to avoid damage to the instrument by bromine or HBr, these species were removed to the fullest extent possible before sampling by the GC. The sampled gas stream was thus composed primarily of residual methane, nitrogen and argon. Gas analysis was performed by an Agilent Quad 400 Micro-GC (Agilent Technologies, Inc., Wilmington, DE). Methane was analyzed by a PoraPlot Q column and methane, argon, and nitrogen were analyzed by a Type 5A molecular sieve column. Several reference gas mixtures containing nitrogen, argon, methane, carbon dioxide and carbon monoxide were used for calibration of the GC and ultrapure helium served as the carrier gas (Matheson Tri-Gas, Fremont, CA).

The GC was also capable of detecting other gases in the reactor exit stream. Higher hydrocarbons, such as ethane, that might have been formed (refer to the computational studies described above) and that have very limited solubility in water could also have been in the gas sampled by the GC. Such saturated hydrocarbons could have been detected by the OV-1 column installed in the GC used for this work. However, no standards were obtained to calibrate that particular column for such gases because very few reactor runs gave any indication of the presence of two-carbon species on the OV-1 column. The molecular sieve column also provided the capability to detect hydrogen. Although the GC method was not calibrated for hydrogen, the detectability limit was less than 0.1%. However, no hydrogen peak was observed on any of the runs reported here. The GC was used occasionally to follow the progress of the decoking operation. The PoraPlot Q column can detect carbon dioxide, while the molecular sieve column can detect carbon monoxide. However, only the peak for CO₂ was observed. Similarly, leaks of air or the presence of oxygen-containing reaction products during reactor runs could have been detected with the GC, but no such leaks were observed in any of the tests.

Analysis of HBr in scrubber solutions

The pH of the solution in the first scrubber was typically 1, or less, while that of the second scrubber was typically at least 3 pH units higher. The aqueous solutions in the scrubbers were analyzed by titration with standardized 0.1N sodium hydroxide solution, using phenolphthalein as an indicator, to determine the amount of HBr collected. In some tests, a small amount of bromine vapor was able to pass the dry ice-IPA trap and was dissolved in the scrubber solution. These solutions had a characteristic light green coloration. Dissolved bromine was reductively titrated with a standard solution of sodium nitrite to prevent it from deactivating the pH indicator. The sodium hydroxide solution was periodically checked against a standard HCl solution to ensure the accuracy of the results. Duplicate titrations were performed on numerous samples to confirm the results.

Gravimetric analysis of reaction products

Several components of the reactor apparatus were weighed before and after the reactor runs to obtain information regarding the mass balances of carbon and bromine. After a run, the reactor tube was cooled and weighed to determine the amount of deposited soot by difference with the initial clean weight. The tube was then reinstalled, reheated, and flushed with air at a temperature in excess of 500°C for a sufficient time to oxidize all the soot accumulated during the experiment. Although the accuracy of some of these weight measurements was limited, this procedure still provided very useful information. The large reactor tube typically did not accumulate enough particulate carbon to allow differential weight measurements at accuracy greater than about 20%. The small reactor tube was more easily manipulated on the laboratory balance and could be weighed more accurately. The amount of soot deposited on the glass wool used to pack the soot collector was determined by differential weight measurements before and after most runs. The glass wool was initially weighed in a tared, anti-static bag to which it was returned after the experiment for a final weight measurement. The cold traps were weighed before and after runs on occasions when material was collected in them. The traps were sealed with threaded PTFE plugs, allowed to warm to room temperature, and thoroughly wiped to remove the external condensation from the laboratory atmosphere before weighing.

Experimental Results and Discussion

The experimental results are summarized in this section and the effects of the most important reactor variables (temperature, reactant feed ratio, residence time) on production of hydrogen bromide are discussed in a general manner. The visual observations of various types of products are presented and the results of material balance calculations for the reactants are summarized. A systematic analysis of the reactor data is presented in a subsequent section of the report that concerns computational reactor modeling. In the computational analysis, a complete description of the operating variables for each run can be input and a single figure-of-merit, e.g., conversion, can be calculated to provide an assessment of the fidelity of the model.

The experimental results are collected in Tables II and III. Table II contains data from experiments that included on-line GC analysis of the output gas stream. These runs were confirmed to have attained steady-state operation, regardless of the range of temperatures or residence times, because the concentration of methane in the trapped and scrubbed exhaust stream was observed to reach a constant value. An example of such behavior is shown in Figure 9, where the methane peak areas determined by the PoraPlot Q and molecular sieve columns in the gas chromatograph attain constant values after several minutes of reactor operation. The data in this figure are the raw areas under the peaks for methane on each of the columns, so the plots do not overlay each other.

The entries in Table II summarize the Run ID number, reactor temperature, reactor volume (cubic centimeters), residence time (seconds at the reactor conditions), and the molar ratio of bromine to methane in the feed stream. The total amount of bromine delivered to the reactor is expressed in terms of millimoles (mmol). The outlet concentration of methane is given in mol%. The balance of the gas stream was nitrogen and argon, which were always present individually in at least ten times the concentration of either of the reactants. The amount of HBr collected during the run by the scrubbers is given in millimoles and is used to calculate the extent of conversion of the stoichiometrically-limiting reactant. In all runs except 0729, including those near the stoichiometric ratio of 2, bromine was the limiting reactant. The stoichiometric ratio is based on the primary reaction shown earlier in Equation (1). The percentage conversion (HBr Yield) was calculated as $100 * (\text{HBr, mmols}) / (2 * \text{Br}_2, \text{mmols})$. The percentage conversion for Run 0729, in which methane was the limiting reactant, was calculated as $100 * (\text{HBr, mmols}) / (4 * \text{CH}_4, \text{mmols})$. Table II summarizes the visual observations regarding the formation of solid carbon (soot) and the presence of unreacted bromine in the reactor effluent. These entries indicate if any material was visible, regardless of quantity.

Table III summarizes data from the preliminary runs which were performed before the GC was placed on-line. These data are presented as corroborating observations based on the chemical analysis of the scrubber contents to determine the yield of HBr as well as observations of soot formation and bromine in the reactor effluent. These data expand upon the behavior of the reactor for methane-rich conditions in which the ratio of bromine to

methane in the feed was less than unity. Table III is organized in the same layout as Table II, except that no entries appear for the exit concentration of methane.

Some comments regarding specific runs are necessary to clarify obvious conflicts in the data presented in the tables. Table II reports that Run 0703 had a conversion exceeding 78%. This entry was made because the outlet tubing developed a leak that allowed some loss of HBr before the line was resealed and all of the exit gases were passed to the scrubbers. Table II also reports that the conversion in Run 0729 exceeded 66%. This entry was made because the excess bromine in the reactor feed dissolved in the scrubbers and interfered with the titration of HBr. The amount of HBr produced was probably underestimated significantly. Table III reports that Run 0423 had a conversion slightly exceeding 100%; obviously this value is somewhat in error. The titration of the scrubber sample was rechecked and produced the same result. The source of error was most likely a discrepancy in measuring the input amount of bromine. Qualitative observations during Run 0423 indicated that soot was formed without any deposit related to unreacted bromine. This suggests a high degree of conversion and we suspect that the true value of conversion was greater than 90%.

Effect of temperature on conversion

The HBr conversion data in Tables II and III is plotted in Figures 10 and 11 in a format that enables the effects of the primary reactor variables to be more easily visualized. Figure 10 shows the extent of conversion to HBr vs. reactor temperature for runs in which methane was present in stoichiometric excess in the reactor feed. All but one datum in this plot correspond to ratios of $\text{Br}_2:\text{CH}_4$ of one or less; the exception was 1.43. Figure 11 is a companion plot of the data for runs in which the reactants were mixed initially in a nearly stoichiometric molar ratio. These values of $\text{Br}_2:\text{CH}_4$ range from 1.8 to 1.9. Figure 11 also displays the single datum for the excess-bromine run (0729), denoted by the filled diamond symbol at a temperature of 800°C . The data for the 80 cm^3 reactor are shown as the half-filled square symbols and the filled circles represent data for the 280 cm^3 reactor. The symbol with the arrow in Figure 10 corresponds to Run 0703 and indicates that this datum is known to be a lower bound on the true value.

Conversion of bromine to HBr ranged from values as high as 95% to as low as 36%. In general, conversion of bromine to HBr increased as the temperature increased. At temperatures near 800°C , conversion was at least 90% for the range of residence times studied here. However, the thermodynamic calculations discussed earlier in the report indicated that the yield of HBr should be essentially 100% at equilibrium when solid carbon is formed as a reaction product. Because soot was observed in all tests at temperatures above 700°C , less than complete conversion implies that reaction kinetics were limiting. Except possibly at the highest temperatures studied, the residence time was not sufficient to approach the equilibrium state closely. The analysis of kinetics is discussed in the section on reactor modeling that follows.

The longer residence times obtained when using the larger reactor usually increased the extent of conversion. This is evident from the plots in Figures 10 and 11 that show that the conversion data corresponding to the large tube generally exceed those for the small tube at

the same temperature. For example, Run 0328 at 680°C in the small reactor tube produced 73% conversion, while 87% was obtained with the large tube; see Run 0403 in Table III. However, the expected dependence of conversion upon residence time was not strictly observed. Residence time was not varied systematically using a single reactor size, but rather fell into two narrowly-grouped ranges depending on which reactor was used. Other factors that are intrinsic to the two reactors, such as the surface area to volume ratio, fluid dynamics, temperature distribution, etc., may have influenced the results to some degree. These factors are considered in further detail in the section on reactor modeling.

The visual observations regarding the formation of solid carbon (soot) and the presence of unreacted bromine in the reactor effluent are summarized in Tables II and III. The formation of soot was obvious and deposits often coated the reactor tube from the beginning of the heated region to the exit joint of the tube. Significant amounts of soot were usually entrained in the flowing gas stream and collected by the glass wool packing in the external chamber. It was ordinarily observed that soot collected in the glass-wool filter shortly after both reactants were admitted, rather than requiring a noticeable induction time. Figure 12 shows a photograph of the 280 cm³ reactor tube coated with a soot deposit. This deposit was formed during Run 0403, which was conducted at 680°C for one hour. At temperatures between 500°C and 600°C, solid carbon was formed in significantly less quantities than in runs at higher temperatures. In this temperature range, soot deposits were observed that did not form completely opaque coatings on the reactor tube walls. Experiments at temperatures above 600°C typically resulted in the formation of significant amounts of soot. Attempts to quantify the amount of soot produced are described in the section on material balances.

If sufficient unreacted bromine exited the reactor, it was observed as solid lenses in the dry ice-IPA trap. These lenses formed a brown vapor upon warming the trap to room temperature. Unreacted bromine was also observed as solid coatings on the FEP tubing that conveyed the reactor effluent into the cold traps. These coatings evaporated fully upon warming to room temperature. In some tests, a small amount of bromine vapor was able to pass the dry ice-IPA trap and dissolved in the scrubber solution. Attempts to quantify the amount of unreacted bromine in several runs are described in the section on material balances.

On a few occasions there were residues observed in the cold traps that did not evaporate upon warming, in contrast to bromine. Liquid residues were observed in the -75°C trap in Run 0613 and Run 0711. A white solid residue was observed in Run 0620. The mass of such trapped material was less than 0.1 gm. These residues could have been one of the single-carbon bromocarbon compounds discussed earlier. Based on the phase transition temperatures mentioned earlier, the liquid residues may have been either dibromomethane or bromoform. The solid residue may have been carbon tetrabromide. The residues were readily soluble in isopropanol, which is consistent with the supposition that they were low molecular weight bromocarbons. Although methyl bromide could have formed, it is unlikely that any was collected in the cold traps, because its vapor pressure is high and its partial pressure would have been reduced by dilution in the sweep gases. Methyl bromide would also have evaporated completely upon warming the trap.

Several tests were conducted at essentially the same temperature and reactant input ratio to demonstrate that the reactor operation was reproducible. The 280 cm³ reactor was operated at, or near, 750°C on three separate days over a period of about two weeks. The input gas composition (mol %) was 4.5 CH₄, 4.4 Br₂, balance nitrogen and argon, so the molar ratio, Br₂/CH₄, was nearly 1. The results of these runs were taken from Table III and summarized below. Runs 0509 and 0522 had conversions above 90%, while 0520 was a bit lower at 83.1%. Run 0520 was conducted at a slightly lower temperature. The titrations of the scrubber solutions were replicated to ensure accuracy. The visual observations of reaction products were also very similar in these tests. These three runs produced considerable amounts of soot in the reactor tube and the glass-wool-packed collector. No unreacted bromine was visible in the exhaust stream or was apparent in the -75°C trap or the aqueous scrubbers. Similarly, no residues were observed in the ice trap. These data indicate that the reactor system could be operated in a reproducible manner.

<u>Test#</u>	<u>Temp.</u>	<u>Conversion</u>
0509	750°C	96.2%
0520	745°C	83.1%
0522	750°C	92.6%

Mass balance results

Material balances for carbon and bromine were performed in a number of experiments to check the self-consistency of reactor operation. A carbon balance (input vs. output) was obtained by weighing the soot-coated reactor tube and glass-wool packing in the particulate collector, before and after the experiment, and comparing that to the difference in input and output of methane based on gas flow rates and composition. A bromine balance was obtained by comparing the bromine input with the output of HBr and unreacted bromine. Bromine input was determined by weighing the bromine bubbler and mist collector before and after a run. Unreacted bromine output was determined by weighing the cold traps (when collection was visually evident), while bromine dissolved in the scrubbers was analyzed by titration, as described above. Bromine exiting the reactor as HBr was analyzed by titration.

The material balance results are collected in Table IV. Good closure of the mass balance was obtained for bromine in most experiments at temperatures above 700°C. Six of the eight runs for which data are reported accounted for approximately 90-95% of the bromine. The run at 650°C (0724) is conspicuously deficient in the bromine balance. The run using excess bromine (0729) resulted in significant bromine dissolved in the scrubber liquor and the high value probably reflects the difficulty in accurately titrating the dissolved bromine by the method used. In contrast, the accounting for carbon was not nearly as complete. This difference reflects the less precise measurements of the mass of soot collected by various pieces of apparatus.

The material balance data imply that other species containing carbon and bromine, i.e., bromomethanes, were probably formed under some reactor operating conditions. These species were not accountable by the methods used here. Formation of bromomethanes is not

unexpected, as discussed in the earlier section regarding thermochemical equilibrium. Visible indications that bromocarbon compounds were formed were evident for several tests as discussed above. However, it was not possible to separate these compounds for quantitative identification or to perform in-situ analysis using the apparatus constructed for these tests. The formation of bromocarbon compounds is an aspect of reactor behavior that needs to be fully understood because of the hazardous nature of these compounds.

Effect of bromine:methane ratio on conversion

The effect of the bromine:methane ratio in the reactor feed on the extent of conversion of the limiting reactant to HBr was not studied as systematically as the effect of temperature. However, comparing the data for several runs in which the other variables were maintained relatively constant indicates the effect of feed ratio. Comparing several runs conducted using the large tube at 700°C (0620, 0626, 0627), it is evident that conversion decreases as the stoichiometric amount of bromine increases. The effect is confounded somewhat by Run 0626, because it had a larger residence time and thus higher conversion is expected from that factor (see Tables II and III). Similarly, tests performed using the 80 cm³ reactor tube at 800°C show higher conversion for methane-rich conditions. Compare Run 0401, 85% at 770°C, and Run 0703, only 78% at 800°C. The results generally support the intuitive expectation that extent of conversion of the limiting reactant, bromine in this case, is enhanced by a relatively higher proportion of the excess reactant.

Evaluation of other factors that may affect reactor performance could not be included in this study. The surface area/volume ratio may be an important factor in reactor design due to the heterogeneous nature of the soot formation reactions. The surface area/volume ratios of the two reactor tubes used here were 4 cm⁻¹ for the small tube and 3.3 cm⁻¹ for the large one and thus did not provide a significant difference for comparison. The surface area of the soot deposits may well involve more than simple geometric ratios of the reactor tube, however. Unfortunately, the surface area of the soot deposits was not measurable. Soot particles entrained in the flowing gas provide additional surface area that was not quantifiable. Using reactor tubes of larger diameter, which reduces the surface/volume ratio, or packing the reactor tubes with quartz pieces, which have a high specific surface area, may have a significant effect on performance.

Related halogenation studies

In contrast to the numerous studies concerning the thermal pyrolysis of bromohalocarbons, related to their use as flame retardants, an extensive literature search showed that the reaction of bromine and methane has received little attention. A preliminary study of the formation of hydrogen bromide by the reaction of bromine, methane and water was performed by the SRT Group.[2] This scheme included water among the reactants in an attempt to convert the carbon in the feed hydrocarbon to carbon dioxide rather than solid carbon. Water may also react with bromine to form additional HBr. The reactor was operated at temperatures as high as 800°C, although only a few experiments were reported. While conversion to HBr was high, the material balance for the reactants and products was not well quantified. Particulate carbon formation was observed in these experiments, despite the introduction of water vapor. This work has been reviewed by the Western Research Institute.[13]

A few studies of the reaction of halogens and hydrocarbons at elevated temperature have been reported, but apparently only one of the bromine-methane system. The primary interest of these studies was to synthesize mono-substituted halocarbon compounds rather than hydrogen bromide. Mock and colleagues employed a catalytic process to prepare [carbon-11]methyl bromide from methane as a precursor for other labeled compounds used in positron emission tomography.[10] These experiments were conducted at temperatures less than 550°C, significantly below the expected operating temperature of an HBr reactor. Mock and colleagues used an ingenious recycle reactor design and observed the formation of the entire series of bromomethanes, although yields favored the formation of methyl bromide at the conditions of their experiments. This work did not report that significant amounts of HBr were formed. The gas-phase chlorination of ethane was studied at temperatures below 450°C and no soot or hydrogen chloride were reported in the products.[14] The gas-phase reaction of iodine and methane was investigated by Link.[15] Experiments were conducted at temperatures below 450°C and no soot or hydrogen iodide were reported in the products. The conversion of methane to methyl iodide was less than 50%.

The three papers cited above indicate that halomethane compounds are formed preferentially to the corresponding hydrogen halide at temperatures below nominally 500°C. However, the information available in the chemical literature provides little guidance concerning the behavior of the reaction of bromine and methane under conditions intended to exhaustively extract hydrogen from methane and produce hydrogen bromide. Our interpretation of the reactor data discussed above is based on computational reactor modeling presented in the following section.

Computational Reactor Analysis

In an attempt to validate the mechanism proposed earlier for HBr production from methane and bromine, the tube flow experiments conducted at SNL have been simulated at various levels of sophistication using the codes available in the CHEMKIN collection. For a given set of process conditions (temperature, pressure, and inlet composition), the equilibrium state was first calculated both with and without solid carbon in the list of candidate species. Because equilibrium is unlikely to be achieved in the reactor, the actual kinetics were then simulated with the plug flow reactor code PLUG, assuming isothermal operation. Again, calculations were carried out both with and without allowance for the formation of solid carbon at the reactor wall. It should be noted, however, that a plug flow simulation involves two assumptions that are highly questionable in the current situation. First, the radial velocity profile is taken to be flat, whereas in reality the Reynolds number is so low that the parabolic profile characteristic of a laminar flow should be used. Second, and more important, radial transport of species is assumed to be rapid relative to the speed of the surface deposition reaction, and this can be true only if the reactive sticking coefficients are no larger than about 10^{-4} . In order to overcome these limitations, simulations involving carbon deposition were also performed using CRESLAF, the boundary layer code in the CHEMKIN package. This kind of calculation is far more difficult and time-consuming than the others, but it should in principle provide the best representation of the true situation in the reactor. By comparing the results of the different types of simulations, one can draw some conclusions about the relative importance of the various processes taking place.

The gas-phase reaction mechanism detailed in Table I was used in the current computations as well. Among the species are 11 carbon-containing radicals, and it was assumed that each of these can react at the surface to deposit solid carbon with a sticking coefficient of unity. The gas-phase products of each deposition reaction were assumed to include HBr to the extent possible, with the remainder being molecular hydrogen or bromine. The resulting surface reaction mechanism is summarized in Table V. Since CRESLAF simulations involve the computation of transport properties, it was necessary to augment the CHEMKIN data base of Lennard-Jones parameters with values for the bromine-containing species. Where these were not available from the literature, values were estimated either from standard correlations or by analogy.

The key results of the computations are summarized in Table VI. For each set of process conditions and for each method of simulation, the table gives three calculated quantities: (a) the percent yield of HBr based on the limiting reactant, which is bromine in all cases but one; (b) the percentage of inlet bromine atoms exiting the reactor in bromocarbon molecules; and (c) the percentage of inlet carbon atoms remaining in the reactor as a solid deposit. For the first of these an experimental value is available, so this is shown in the table as well. Fortunately, this quantity seems to be fairly sensitive to the process conditions, so it should be useful in assessing the merits of the different modeling approaches.

The first conclusion to be drawn from Table VI is that the yield of HBr is always increased when allowance is made for the formation of solid carbon, whether in the equilibrium or the

plug flow computations. In fact, since CRESLAF and PLUG give essentially identical results when there is no carbon deposition, it can be seen that this conclusion holds for CRESLAF as well. Of course, this is not a surprising observation, since a 100% yield of HBr would require *all* of the carbon to be in solid form if the reactants were in stoichiometric proportions. The results in the table show that the converse statement, namely that carbon deposition enhances the HBr yield, is true as well. This is a reflection of the thermodynamic stability of HBr relative to its constituent elements.

Turning to the comparison of modeling and experiment, the most obvious conclusion is that the experimental reactor conversion is in all cases smaller than the unconstrained equilibrium value, i.e., the value with solid carbon included in the calculation. Therefore, the residence time in the reactor is never sufficient to allow the process to reach equilibrium. At low and moderate temperatures, the experimental conversion falls short of the equilibrium value even when solid carbon is deleted from the calculation. Presumably, the amount of soot formed under these conditions is sufficiently small that the effect of the finite residence time still dominates. However, at the highest temperatures, the effect of soot formation becomes important enough that the experimental conversion can exceed the constrained equilibrium value in spite of the finite residence time. This is a clear indication that heterogeneous chemistry is of crucial importance in this process.

Next, it can be seen that the experimental conversion at the lowest temperatures is somewhat smaller than the value predicted by gas-phase kinetics alone, i.e., by the PLUG calculation with solid carbon omitted. In theory this should not happen, and the reasons for the shortfall are not entirely clear, but the most likely explanation is that the experimental values are slightly low due to the inability to sweep out all of the HBr generated by the process. Fortunately, the discrepancies are generally small. At temperatures exceeding 700°C, on the other hand, the experimental conversion always exceeds the gas-kinetic value by a comfortable margin, presumably because soot formation is taking place at a substantial rate.

If one attempts to account for soot formation in the PLUG calculation by allowing the gas-phase radicals to react at the tube wall with a sticking coefficient of unity, then the experimental HBr yield is always overpredicted, as shown in the table. It might be concluded from this that the sticking coefficient is simply too large. However, the computation itself is inconsistent, because the lack of radial concentration gradients in the plug flow model means that the resistance to radial transport of the radicals by diffusion is being neglected. The Damkohler number based on a sticking coefficient of unity is found to be roughly 10^4 , so in actuality the resistance to diffusion is much greater than that due to the surface reaction, and the plug flow model is a poor approximation. Since the sticking coefficient would have to be reduced by several orders of magnitude in order to remedy this, and since this would effectively eliminate the carbon deposition, the only real option is to abandon the plug flow model in favor of one that accurately accounts for the radial diffusion.

The final comparison, then, is between the experimental conversions and those predicted by the laminar boundary layer code CRESLAF, again using a sticking coefficient of unity. It can be shown that the average deviation using CRESLAF is indeed smaller than for any of the

other modeling options, in either a simple mean or root-mean-square sense. Still, there are some significant discrepancies. The computed conversion tends to be somewhat high at low temperatures and low at moderate temperatures, and it is very high when bromine is in excess. The overprediction at low temperatures is very similar to that for the gas-only PLUG calculation, because very little carbon deposition is taking place. Again, artificially low experimental values are the most likely cause. The underprediction at higher temperatures is somewhat more pronounced; it seems that CRESLAF is underestimating the amount of soot formation at the same time that PLUG overestimates it. Fortunately, there is a plausible physical explanation for this: A significant amount of soot may be formed in the interior of the reactor rather than at the walls. In fact, the filters installed downstream of the reactor tube did collect readily observable amounts of soot, as reported above. The formation of these particles is a pseudo-homogeneous process that the current CRESLAF-based model cannot simulate. If it could, then the predicted rate of soot production would increase due to both an increased surface area for deposition and a decreased resistance to diffusion of depositing radicals. Relying once again on the premise that carbon production and HBr yield are closely linked, one can surmise that the additional soot formation would bring the predicted reactor conversions more into line with the experimental values.

The apparent overprediction of the HBr yield by CRESLAF in the excess-bromine case is an obvious exception to the trend just discussed. This may indicate a fundamental flaw in the chemical mechanism; however, an artificially low experimental value is a more likely explanation, for the following reasons. As noted in the preceding section, there are experimental difficulties involved in titrating HBr when dissolved bromine is present, and this could cause the yield of HBr to be underestimated. Consistent with this, the measured amounts of HBr and Br₂ in the effluent stream together account for only 61% of the bromine fed to the reactor. If these numbers are accurate, then the remaining bromine must have exited the reactor in the form of bromocarbon molecules, meaning that a substantial amount of carbon must have done the same. This is unlikely, however, because the measured amount of soot actually exceeded the amount of carbon fed to the reactor, as reported in Table IV. The fact that soot formation was particularly intense in this case lends some support to the CRESLAF simulation, as can be seen from the last section of Table VI.

Even though there are no quantitative experimental results on the formation of bromocarbon molecules, it is interesting to examine the predictions of the models with regard to these species. First, the bromocarbons are completely absent in an equilibrium mixture, and this remains nearly true even when solid carbon is excluded. Therefore, the production of these undesirable compounds is a theoretically avoidable kinetic phenomenon. The results from the PLUG calculations show that the propensity for these species to form in the gas phase is quite strong and is remarkably insensitive to temperature. It can be effectively suppressed by the alternative process of carbon formation, but this occurs readily only at high temperatures. This, in turn, is probably due to the fact that the pool of reactive radicals becomes more populous at high temperatures. In any case, the CRESLAF results suggest that the amounts of bromocarbons being formed under the experimental conditions are appreciable even at the highest temperatures, although the numbers in Table VI are probably somewhat high, and the excess bromine case is again an exception. Qualitative indications of the presence of some

bromocarbons in the reactor effluent have in fact been observed, as discussed earlier. Therefore, it will be advantageous to do whatever possible to accelerate the rate of soot formation, perhaps by increasing the internal surface area, and thereby minimize the appearance of the unwanted byproducts. Alternatively, the use of excess bromine instead of methane may help to achieve the same objective.

Summary



A compact tubular reactor was used to measure the extent of conversion and the kinetics of the reaction of bromine and methane that yields hydrogen bromide as the primary product. Experiments were conducted at temperatures between 500°C and 800°C with inlet mixtures containing excess methane, near-stoichiometric amounts of reactants, and excess bromine. The residence time for the reaction was varied mainly by using reactor tubes of two different sizes, although a lesser variation was also achieved by changing the flow rate of reactants. Quantitative conversion of bromine to hydrogen bromide was observed at temperatures above 750°C. Similarly, conversion of methane to soot was observed at temperatures above 650°C. Experiments at temperatures below 600°C tended to produce little or no soot.

Computational chemistry modeling of the kinetics of this reaction was performed to interpret the reactor data. An elementary multistep mechanism for the gas-phase chemistry was used both with and without a surface mechanism that assumed deposition of radical species at the reactor walls. Simulations were carried out with the plug-flow and boundary-layer codes in the Sandia CHEMKIN package. The calculations showed that equilibrium conversions cannot be expected within reasonable reactor residence times. However, the simulations obtained reasonably good agreement with the experimental data, using the conversion to hydrogen bromide as the primary measure of product speciation.

At temperatures below 750°C, observations of the contents of the cold traps clearly indicated that bromocarbon compounds were formed, although neither the identities nor the concentrations of these species could be determined with the apparatus used for these experiments. The experimental material balance data imply that such species were also formed to a significant extent at 800°C, the highest temperature studied. Similarly, the computational reactor simulations indicate that bromocarbon compounds may be expected over a wide range of reactor operating conditions. The formation of bromocarbon compounds is an aspect of reactor behavior that needs to be fully understood before further development because of the hazardous nature of these compounds.

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Figures

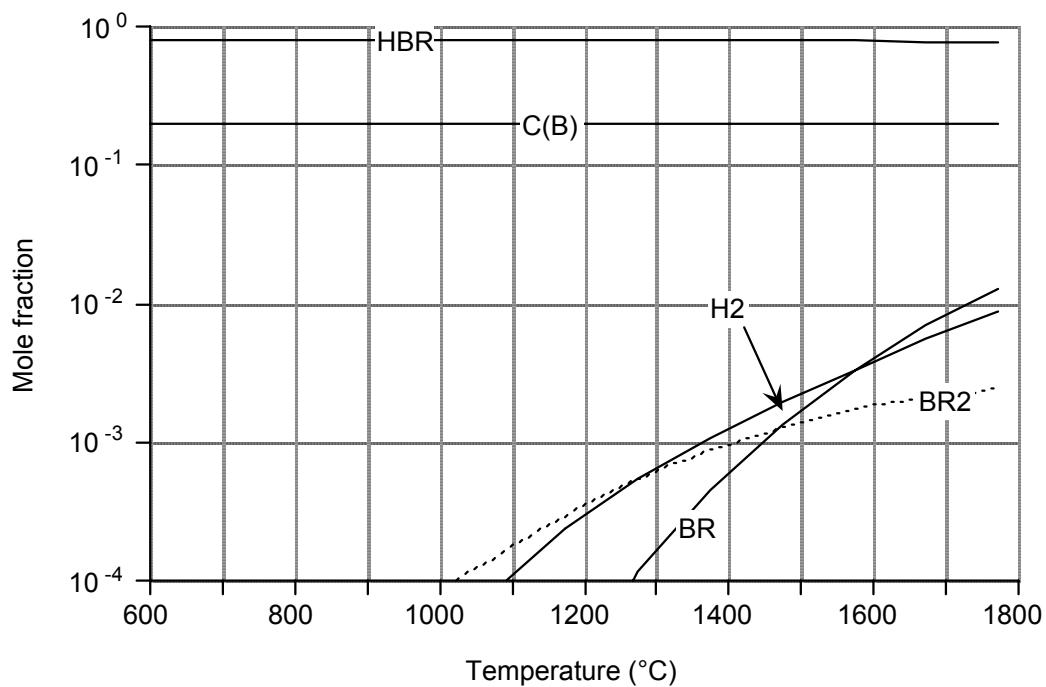


Figure 1. Equilibrium composition for $\text{CH}_4 + 2 \text{Br}_2$ at 1 atm and various temperatures.

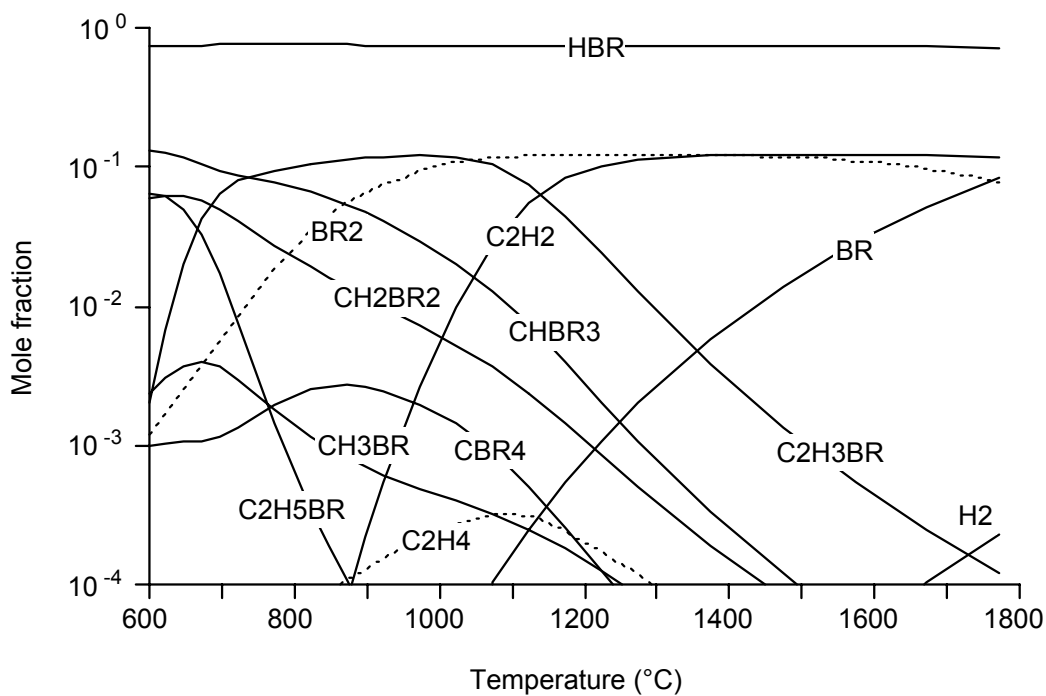
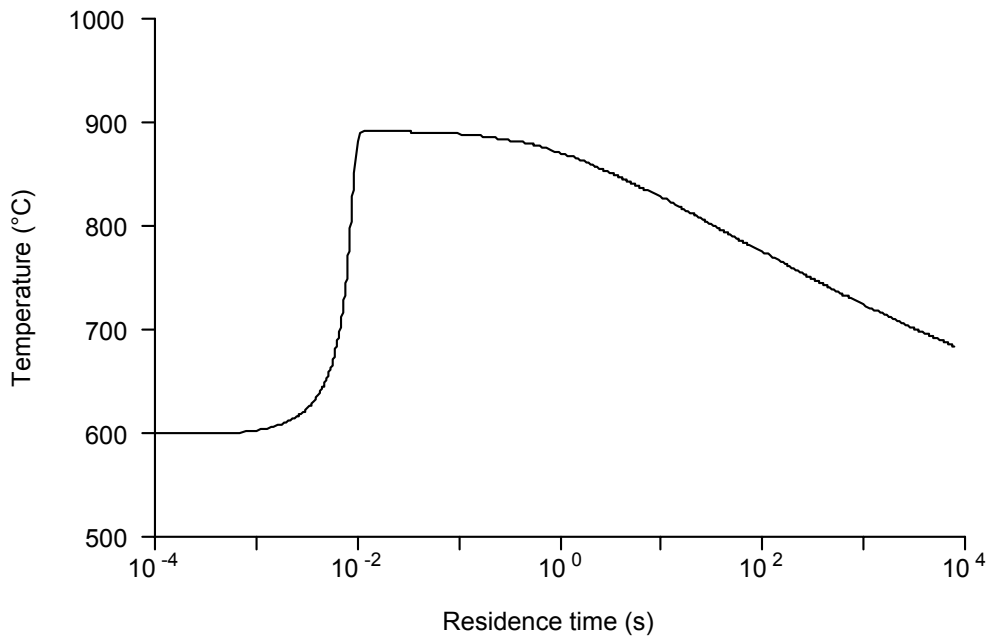
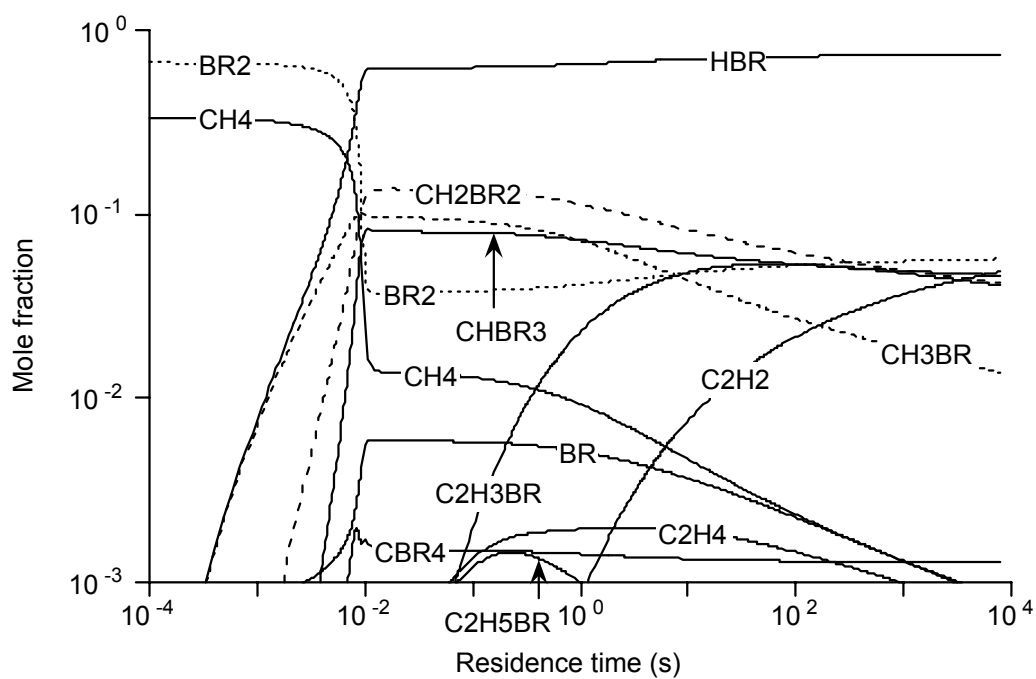


Figure 2. Equilibrium composition for $\text{CH}_4 + 2 \text{Br}_2$ at 1 atm and various temperatures (solid carbon not included).



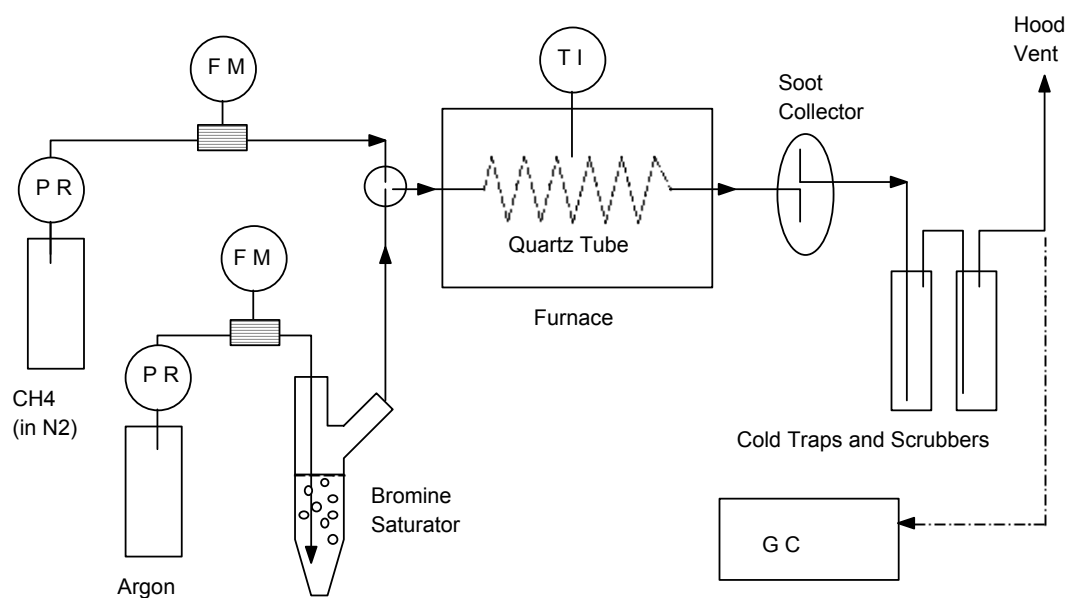


Figure 5. Schematic diagram (upper) and a photograph (lower) of the bromine-methane reactor apparatus assembled in the fume hood.



Figure 6. Photo of bromine saturator device (at left, with 3 arms) and second stage demister (at right, with 2 arms) in the ice bath.

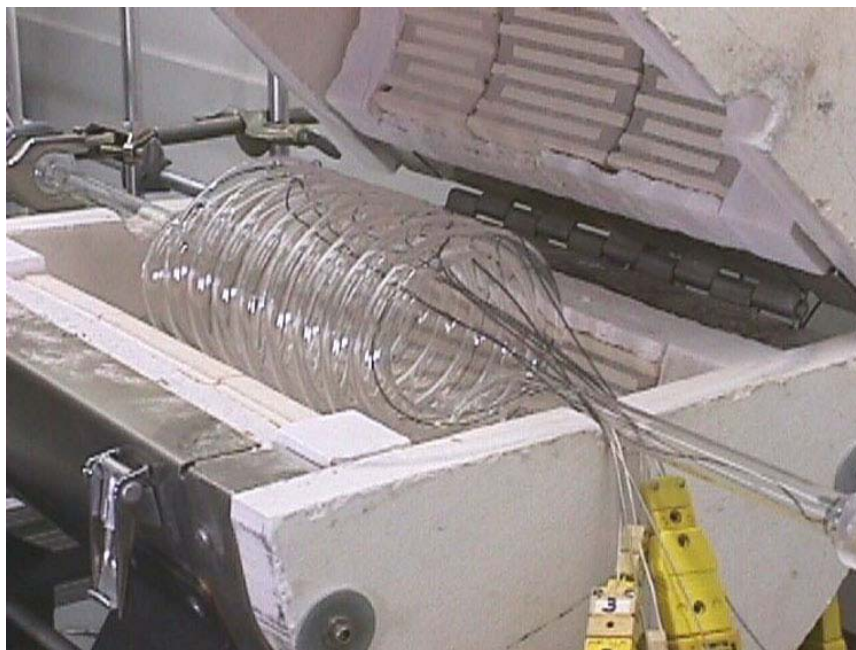


Figure 7. Photo of large-volume quartz reactor tube showing thermocouples used to monitor temperatures during operation.

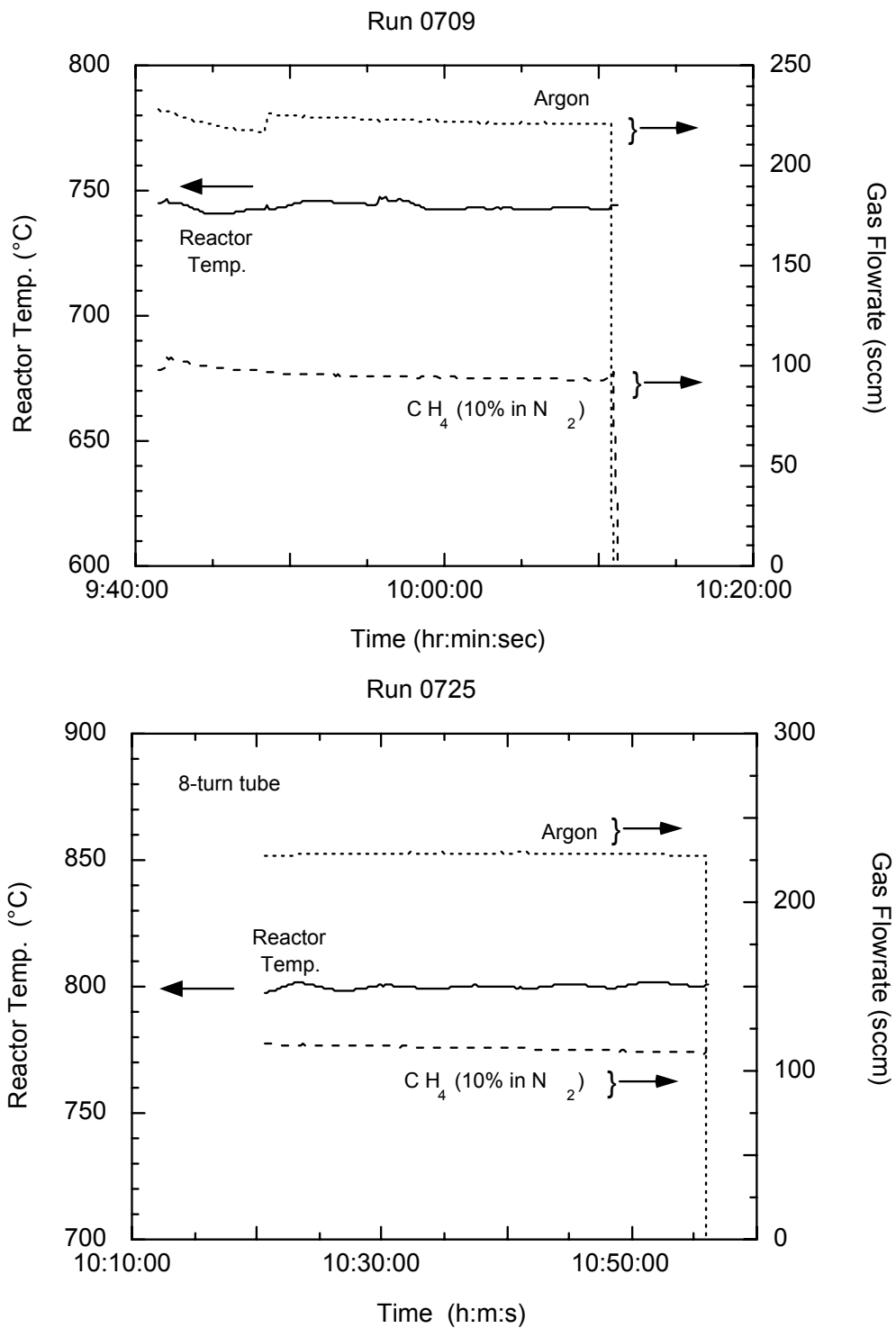


Figure 8. Representative plots of reactor temperature and mass flow rates during bromine-methane reactor runs 0709 and 0725.

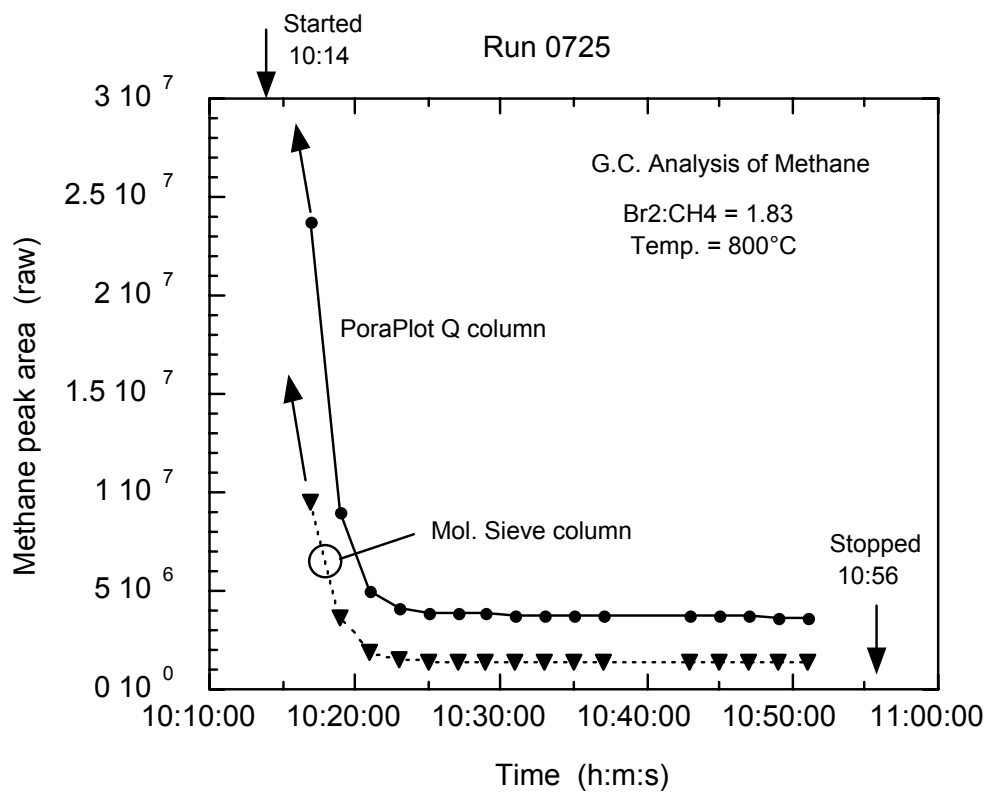


Figure 9. Representative plot of gas chromatograph analysis of methane concentration by two columns that shows the attainment of steady-state conditions in the reactor.

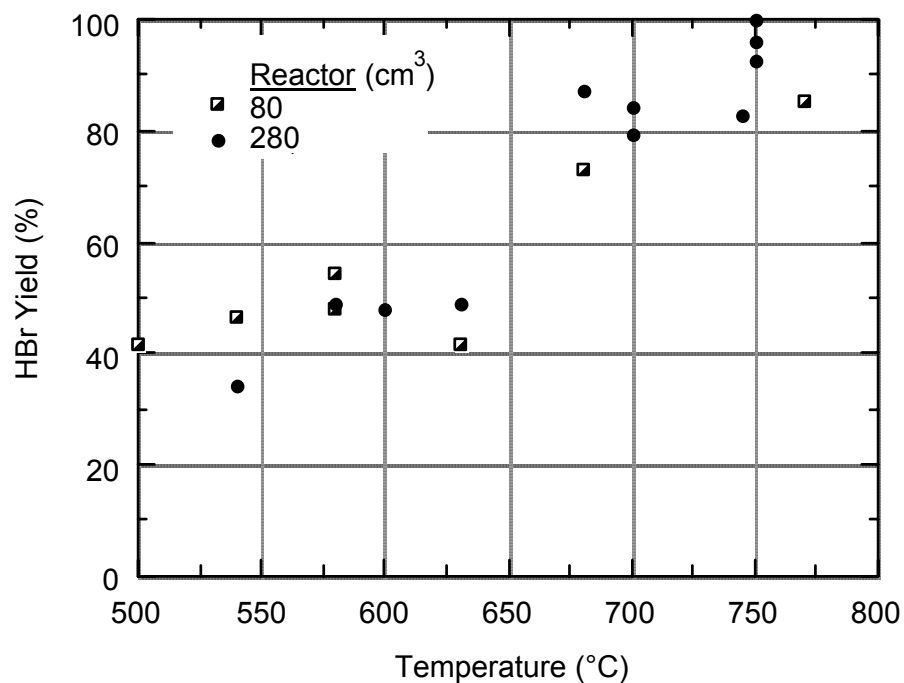


Figure 10. Effect of temperature on conversion (yield) of bromine to hydrogen bromide for runs in which methane was present in stoichiometric excess.

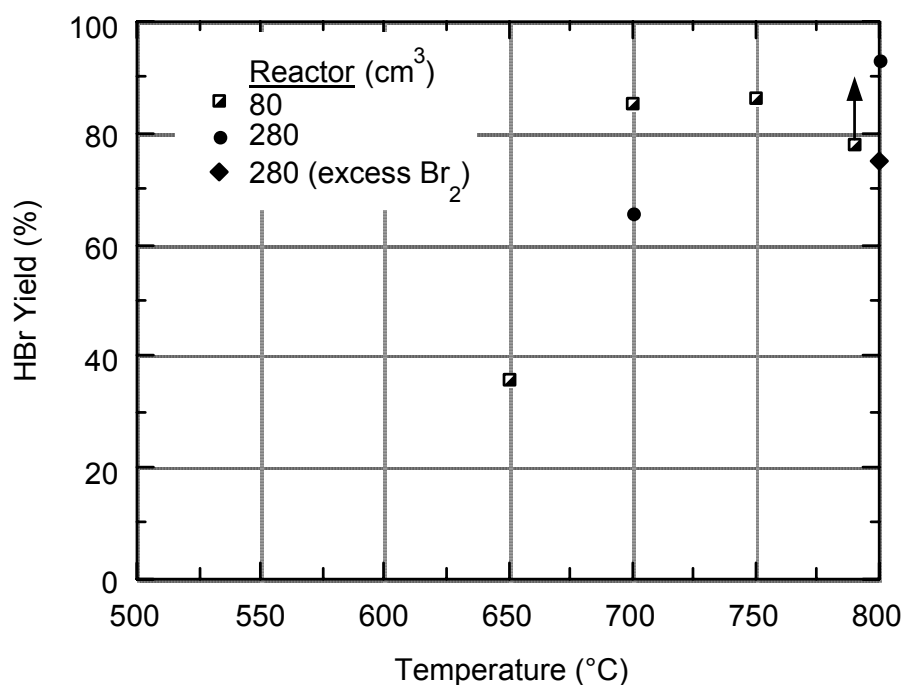


Figure 11. Effect of temperature on conversion of bromine to hydrogen bromide for runs in which bromine and methane were present in nearly stoichiometric amounts.



Figure 12. Photo of carbon deposit on walls of quartz reactor tube resulting from reacting bromine and methane at 680°C for 1 hour. Methane was present in stoichiometric excess.

Tables

Table I. Gas-phase reaction mechanism for methane-bromine process.
(Temperature units are Kelvin.)

CHEMKIN-III GAS-PHASE MECHANISM INTERPRETER:
DOUBLE PRECISION Vers. 6.16 98/08/15
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		ELEMENTS CONSIDERED		ATOMIC WEIGHT							
		1. H		1.00797							
		2. C		12.0112							
		3. BR		79.9009							
		4. N		14.0067							
		5. AR		39.9480							
SPECIES CONSIDERED		P H A S E	C H A R G E	MOLECULAR WEIGHT	TEMPERATURE		ELEMENT COUNT				
					LOW	HIGH	H	C	BR	N	AR
1. H2		G	0	2.01594	200	3500	2	0	0	0	0
2. H		G	0	1.00797	200	3500	1	0	0	0	0
3. C		G	0	12.01115	200	3500	0	1	0	0	0
4. CH		G	0	13.01912	200	3500	1	1	0	0	0
5. CH2		G	0	14.02709	200	3500	2	1	0	0	0
6. CH2(S)		G	0	14.02709	200	3500	2	1	0	0	0
7. CH3		G	0	15.03506	200	3500	3	1	0	0	0
8. CH4		G	0	16.04303	200	3500	4	1	0	0	0
9. C2H		G	0	25.03027	200	3500	1	2	0	0	0
10. C2H2		G	0	26.03824	200	3500	2	2	0	0	0
11. C2H3		G	0	27.04621	200	3500	3	2	0	0	0
12. C2H4		G	0	28.05418	200	3500	4	2	0	0	0
13. C2H5		G	0	29.06215	200	3500	5	2	0	0	0
14. C2H6		G	0	30.07012	200	3500	6	2	0	0	0
15. BR		G	0	79.90090	300	5000	0	0	1	0	0
16. BR2		G	0	159.80180	300	5000	0	0	2	0	0
17. HBR		G	0	80.90887	300	5000	1	0	1	0	0
18. CH3BR		G	0	94.93596	300	1501	3	1	1	0	0
19. CH2BR		G	0	93.92799	300	1501	2	1	1	0	0
20. C2H5BR		G	0	108.96305	300	3000	5	2	1	0	0
21. C2H3BR		G	0	106.94711	300	3000	3	2	1	0	0
22. CH2BR2		G	0	173.82889	300	1501	2	1	2	0	0
23. CHBR3		G	0	252.72182	300	1501	1	1	3	0	0
24. CHBR2		G	0	172.82092	300	1501	1	1	2	0	0
25. CBR4		G	0	331.61475	300	1501	0	1	4	0	0
26. CBR3		G	0	251.71385	300	1501	0	1	3	0	0
27. N2		G	0	28.01340	300	5000	0	0	0	2	0
28. AR		G	0	39.94800	300	5000	0	0	0	0	1

$$(k = A T^{**}b \exp(-E/RT))$$

REACTIONS CONSIDERED				A	b	E
1.	2H+M<=>H2+M			1.00E+18	-1.0	0.0
	H2	Enhanced by	0.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
2.	2H+H2<=>2H2			9.00E+16	-0.6	0.0
3.	H+CH<=>C+H2			1.10E+14	0.0	0.0
4.	H+CH2(+M)<=>CH3(+M)			2.50E+16	-0.8	0.0
	Low pressure limit: 0.32000E+28 -0.31400E+01 0.12300E+04					
	TROE centering: 0.68000E+00 0.78000E+02 0.19950E+04 0.55900E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
5.	H+CH2(S)<=>CH+H2			3.00E+13	0.0	0.0
6.	H+CH3(+M)<=>CH4(+M)			1.27E+16	-0.6	383.0
	Low pressure limit: 0.24770E+34 -0.47600E+01 0.24400E+04					
	TROE centering: 0.78300E+00 0.74000E+02 0.29410E+04 0.69640E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
7.	H+CH4<=>CH3+H2			6.60E+08	1.6	10840.0
8.	H+C2H(+M)<=>C2H2(+M)			1.00E+17	-1.0	0.0
	Low pressure limit: 0.37500E+34 -0.48000E+01 0.19000E+04					
	TROE centering: 0.64640E+00 0.13200E+03 0.13150E+04 0.55660E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
9.	H+C2H2(+M)<=>C2H3(+M)			5.60E+12	0.0	2400.0
	Low pressure limit: 0.38000E+41 -0.72700E+01 0.72200E+04					
	TROE centering: 0.75070E+00 0.98500E+02 0.13020E+04 0.41670E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
10.	H+C2H3(+M)<=>C2H4(+M)			6.08E+12	0.3	280.0
	Low pressure limit: 0.14000E+31 -0.38600E+01 0.33200E+04					
	TROE centering: 0.78200E+00 0.20750E+03 0.26630E+04 0.60950E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
11.	H+C2H3<=>H2+C2H2			3.00E+13	0.0	0.0
12.	H+C2H4(+M)<=>C2H5(+M)			1.08E+12	0.5	1820.0
	Low pressure limit: 0.12000E+43 -0.76200E+01 0.69700E+04					
	TROE centering: 0.97530E+00 0.21000E+03 0.98400E+03 0.43740E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
13.	H+C2H4<=>C2H3+H2			1.32E+06	2.5	12240.0
14.	H+C2H5(+M)<=>C2H6(+M)			5.21E+17	-1.0	1580.0
	Low pressure limit: 0.19900E+42 -0.70800E+01 0.66850E+04					
	TROE centering: 0.84220E+00 0.12500E+03 0.22190E+04 0.68820E+04					
	H2	Enhanced by	2.000E+00			
	CH4	Enhanced by	2.000E+00			
	C2H6	Enhanced by	3.000E+00			
15.	H+C2H5<=>H2+C2H4			2.00E+12	0.0	0.0
16.	H+C2H6<=>C2H5+H2			1.15E+08	1.9	7530.0
17.	C+CH2<=>H+C2H			5.00E+13	0.0	0.0
18.	C+CH3<=>H+C2H2			5.00E+13	0.0	0.0
19.	CH+H2<=>H+CH2			1.11E+08	1.8	1670.0
20.	CH+CH2<=>H+C2H2			4.00E+13	0.0	0.0
21.	CH+CH3<=>H+C2H3			3.00E+13	0.0	0.0
22.	CH+CH4<=>H+C2H4			6.00E+13	0.0	0.0

23.	CH2+H2<=>H+CH3	5.00E+05	2.0	7230.0
24.	2CH2<=>H2+C2H2	3.20E+13	0.0	0.0
25.	CH2+CH3<=>H+C2H4	4.00E+13	0.0	0.0
26.	CH2+CH4<=>2CH3	2.46E+06	2.0	8270.0
27.	CH2(S)+H2<=>CH3+H	7.00E+13	0.0	0.0
28.	CH2(S)+CH3<=>H+C2H4	1.20E+13	0.0	-570.0
29.	CH2(S)+CH4<=>2CH3	1.60E+13	0.0	-570.0
30.	CH2(S)+C2H6<=>CH3+C2H5	4.00E+13	0.0	-550.0
31.	2CH3(+M)<=>C2H6(+M)	2.12E+16	-1.0	620.0
Low pressure limit: 0.17700E+51 -0.96700E+01 0.62200E+04				
TROE centering: 0.53250E+00 0.15100E+03 0.10380E+04 0.49700E+04				
H2		Enhanced by	2.000E+00	
CH4		Enhanced by	2.000E+00	
C2H6		Enhanced by	3.000E+00	
32.	2CH3<=>H+C2H5	4.99E+12	0.1	10600.0
33.	CH3+C2H4<=>C2H3+CH4	2.27E+05	2.0	9200.0
34.	CH3+C2H6<=>C2H5+CH4	6.14E+06	1.7	10450.0
35.	C2H+H2<=>H+C2H2	4.07E+05	2.4	200.0
36.	C2H4(+M)<=>H2+C2H2(+M)	8.00E+12	0.4	88770.0
Low pressure limit: 0.70000E+51 -0.93100E+01 0.99860E+05				
TROE centering: 0.73450E+00 0.18000E+03 0.10350E+04 0.54170E+04				
H2		Enhanced by	2.000E+00	
CH4		Enhanced by	2.000E+00	
C2H6		Enhanced by	3.000E+00	
37.	BR+BR+M=BR2+M	1.92E+14	0.0	-1700.0
BR2		Enhanced by	1.400E+01	
CH4		Enhanced by	1.500E+00	
38.	BR+H+M=HBR+M	4.78E+21	-2.0	511.0
39.	HBR+H=BR+H2	1.26E+10	1.1	160.0
40.	BR2+H=BR+HBR	2.28E+11	1.0	440.0
41.	CH3+HBR=CH4+BR	9.46E+11	0.0	-380.0
42.	C2H5+HBR=C2H6+BR	1.02E+12	0.0	-1000.0
43.	CH3BR+H=CH3+HBR	5.11E+13	0.0	5840.0
44.	CH3BR+CH3=CH4+CH2BR	1.26E+12	0.0	10100.0
45.	CH3+BR2=CH3BR+BR	1.21E+13	0.0	-390.0
46.	CH3BR+BR=CH2BR+HBR	1.00E+14	0.0	16310.0
47.	CH3+BR=CH2+HBR	1.10E+14	0.0	22968.0
48.	CH2BR+BR=CH2+BR2	5.00E+09	0.0	10200.0
49.	C2H5+BR2=C2H5BR+BR	1.57E+13	0.0	-820.0
50.	C2H5BR+H=C2H5+HBR	1.00E+14	0.0	5000.0
51.	C2H3BR+H=C2H3+HBR	1.00E+14	0.0	6000.0
52.	C2H3+BR2=C2H3BR+BR	3.02E+13	0.0	-477.0
53.	CH2BR+C2H6=CH3BR+C2H5	1.00E+12	0.0	8500.0
54.	CH2BR+C2H4=C2H3+CH3BR	2.00E+12	0.0	12000.0
55.	CH2BR+CH3=C2H5BR	3.10E+11	0.0	-4300.0
56.	CH2BR+CH3=C2H4+HBR	5.40E+12	0.0	1400.0
57.	CH2BR+CH3=C2H5+BR	1.00E+13	0.0	7000.0
58.	CH2BR+H2=CH3BR+H	2.00E+12	0.0	13100.0
59.	C2H5+BR=C2H5BR	2.00E+13	0.0	0.0
60.	C2H3+BR=C2H3BR	3.00E+13	0.0	0.0
61.	BR+C2H4=C2H3+HBR	5.00E+12	0.0	25000.0
62.	C2H5BR+CH3=C2H5+CH3BR	1.00E+13	0.0	6000.0
63.	C2H3BR+CH3=C2H3+CH3BR	1.00E+13	0.0	11000.0
64.	CH3+CBR4=CH3BR+CBR3	1.48E+14	0.0	7900.0
65.	CH3BR=CH3+BR	1.58E+14	0.0	71700.0
66.	CH2BR2=CH2BR+BR	1.00E+14	0.0	65600.0
67.	CHBR3=CHBR2+BR	1.58E+14	0.0	59000.0
68.	CBR4=CBR3+BR	2.00E+14	0.0	52400.0
69.	CHBR3+CH3=CBR3+CH4	2.31E+13	0.0	7300.0
70.	CH2BR2+H=CH2BR+HBR	5.11E+13	0.0	5840.0
71.	CHBR3+H=CHBR2+HBR	5.11E+13	0.0	5840.0
72.	CBR4+H=CBR3+HBR	5.11E+13	0.0	5840.0
73.	CH2BR2+BR=CH2BR+BR2	1.82E+14	0.0	24513.0

74. CHBR3+BR=CHBR2+BR2	1.82E+14	0.0	24513.0
75. CBR4+BR=CBR3+BR2	1.82E+14	0.0	24513.0
76. CH2BR2+BR=CHBR2+HBR	1.00E+14	0.0	16310.0
77. CHBR3+BR=CBR3+HBR	1.00E+14	0.0	16310.0
78. CH2BR2+H=CHBR2+H2	1.36E+14	0.0	11964.0
79. CHBR3+H=CBR3+H2	1.36E+14	0.0	11964.0

NOTE: A units mole-cm-sec-K, E units cal/mole

NO ERRORS FOUND ON INPUT:
ASCII Vers. 1.0 CHEMKIN linkfile chem.asc written.

WORKING SPACE REQUIREMENTS ARE
 INTEGER: 2459
 REAL: 1524
 CHARACTER: 33
 Total CPUtime (sec): 5.86E-02

Table II. Operating parameters, gas analysis data, and HBr production results for the Bromine-Methane reactor.

Run ID#	Temp. (°C)	Reactor Volume (cm ³)	Resid. Time (sec)	Br ₂ :CH ₄ Feed (molar)	Br ₂ Input (mmol)	CH ₄ Out (mol%)	HBr Out (mmol)	HBr Yield (%)	Material in Effluent	
									Soot	Br ₂
0522	750	280	22.2	1.00	18.9	1.84	35.1	92.6	Yes	N.V.
0610	540	80	6.8	0.97	20.1	1.61	18.7	46.4	Yes	Yes
0611	580	80	6.6	0.96	20.8	1.34	20.0	48.0	some	Yes
0612	540	280	25.0	0.97	16.9	1.28	11.6	34.3	N.V.	N.V.
0613	580	280	27.0	0.99	20.7	1.23	20.3	49.2	Yes	N.V.
0619	600	280	17.3	0.81	21.3	1.7	20.4	47.9	Yes	Yes
0620	700	280	15.4	0.79	20.4	2.28	32.3	79.2	Yes	N.V.
0626	700	280	19.9	1.43	22.9	0.84	38.8	84.5	Yes	Yes
0627	700	280	16.2	1.81	25.4	0.23	33.5	65.8	Yes	Yes
0703(a)	790	80	4.2	1.74	28.1	0.062	> 43	> 78	Yes	Yes
0709	750	80	4.5	1.90	24.8	0.24	42.8	86.4	Yes	Yes
0711	700	80	4.8	1.81	28.1	0.27	36.9	85.1	Yes	Yes
0724	650	80	4.9	1.87	25.5	0.56	18.1	35.6	Yes	Yes
0725	800	280	14.5	1.83	36.3	0.48	67.7	93.3	Yes	N.V.
0729(b)	800	280	13.5	2.45	48.9	n.d.	26.4	> 66	Yes	Yes

N.V. not visible n.d. not detected

(a) Calculated yield was low because some HBr was lost through a leaking O-ring.

(b) Yield based on methane input (9.9 mmol), which was the limiting reactant.

Table III. Operating parameters and HBr production results for preliminary runs of the Bromine-Methane reactor.

Run ID#	Temp. (°C)	Reactor Volume (cm ³)	Residence Time (sec)	Br ₂ :CH ₄ Feed (molar)	Br ₂ In (mmol)	HBr Out (mmol)	HBr Yield (%)	Materials in Effluent	
								Soot	Br ₂
0321(a)	630	80	8.3	0.56	15.6	12.6	41.6	Yes	N.V.
0327	580	80	7.8	0.63	17.2	18.7	54.2	Yes	Yes
0328	680	80	7.4	0.63	17.3	25.1	72.8	Yes	N.V.
0401	770	80	6.9	0.62	10.2	17.4	85.3	Yes	N.V.
0403	680	280	26.6	0.62	12.0	21.0	87.1	Yes	N.V.
0410	630	280	28.1	0.62	16.8	16.4	48.4	Yes	N.V.
0423	750	280	24.9	0.62	16.8	34.1	101.	Yes	N.V.
0509	750	280	19.3	0.97	18.3	35.4	96.2	Yes	N.V.
0520	745	280	19.3	0.97	17.9	29.7	83.0	Yes	N.V.
0606	500	80	7.1	0.97	13.9	11.6	41.7	N.V.	Yes

N.V. not visible

(a) Scrubbers did not have gas dispersion tubes in this test. Absorption of HBr may have been low.

Table IV. Material balance results for the Bromine-Methane reactor. Quantities of chemical species are given in mmol.

Run ID#	Temp. (°C)	CH ₄ Input	CH ₄ Out	Carbon Out (soot)	% C Out/In	Br ₂ Input	HBr Out	Br ₂ Out (cold trap)	Br ₂ Out (scrubber)	% Br ₂ Out/In
0626	700	16.1	3.7	2.4	38.2	22.9	38.8	1.3	0.0	90.0
0627	700	14.1	1.0	8.3	66.7	25.4	33.5	0.0	7.9	96.7
0703	790	15.6	0.32	17.6	115.	28.1	43.8	0.6	5.4	99.8
0709	750	13.2	1.1	13.9	114.	24.8	42.8	0.6	0.0	89.0
0711	700	15.8	1.4	18.3	124.	28.0	47.7	1.0	1.5	94.1
0724	650	13.7	2.6	10.3	93.8	25.5	18.1	1.6	4.1	57.7
0725	800	19.9	3.1	10.9	70.5	36.3	67.7	0.0	0.0	93.3
0729	800	10.0	0.0	17.3	173.	48.9	26.4	1.7	12.4	112.

Table V. Surface reaction mechanism for methane-bromine process.
(Temperature units are Kelvin.)

CHEMKIN-III SURFACE MECHANISM INTERPRETER:

DOUBLE PRECISION Vers. 7.23 00/03/28

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SPECIES	MOLECULAR			ELEMENT COUNT					
CONSIDERED	WEIGHT	Density	Nsites	H	C	BR	N	AR	

Gas phase species:									
1. H2	2.01594			2	0	0	0	0	
2. H	1.00797			1	0	0	0	0	
3. C	12.01115			0	1	0	0	0	
4. CH	13.01912			1	1	0	0	0	
5. CH2	14.02709			2	1	0	0	0	
6. CH2(S)	14.02709			2	1	0	0	0	
7. CH3	15.03506			3	1	0	0	0	
8. CH4	16.04303			4	1	0	0	0	
9. C2H	25.03027			1	2	0	0	0	
10. C2H2	26.03824			2	2	0	0	0	
11. C2H3	27.04621			3	2	0	0	0	
12. C2H4	28.05418			4	2	0	0	0	
13. C2H5	29.06215			5	2	0	0	0	
14. C2H6	30.07012			6	2	0	0	0	
15. BR	79.90090			0	0	1	0	0	
16. BR2	159.80180			0	0	2	0	0	
17. HBR	80.90887			1	0	1	0	0	
18. CH3BR	94.93596			3	1	1	0	0	
19. CH2BR	93.92799			2	1	1	0	0	
20. C2H5BR	108.96305			5	2	1	0	0	
21. C2H3BR	106.94711			3	2	1	0	0	
22. CH2BR2	173.82889			2	1	2	0	0	
23. CHBR3	252.72182			1	1	3	0	0	
24. CHBR2	172.82092			1	1	2	0	0	
25. CBR4	331.61475			0	1	4	0	0	
26. CBR3	251.71385			0	1	3	0	0	
27. N2	28.01340			0	0	0	2	0	
28. AR	39.94800			0	0	0	0	1	
BULK: BULK1									
29. C(B)	12.01115	0.227E+01	g/cm**3	0	1	0	0	0	

				(k = A T**b exp(-E/RT)					
SURFACE REACTIONS CONSIDERED				A	b		E		

1. C<=>C(B)	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
2. CH<=>C(B)+0.5H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
3. CH2<=>C(B)+H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
4. CH2(S)<=>C(B)+H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
5. CH3<=>C(B)+1.5H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
6. C2H<=>2C(B)+0.5H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
7. C2H3<=>2C(B)+1.5H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
8. C2H5<=>2C(B)+2.5H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
9. CH2BR<=>C(B)+HBR+0.5H2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
10. CHBR2<=>C(B)+HBR+0.5BR2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			
11. CBR3<=>C(B)+1.5BR2	1.00E+00	0.0	0.0
Coefficients are sticking parameters...			

NOTE: A units moles, E units cal/mole
 Default Motz-Wise correction to sticking coefficients is turned ON.

NO ERRORS FOUND ON INPUT:
 ASCII Version 1.5 surface linkfile surf.asc written.

WORKING SPACE REQUIREMENTS ARE
 INTEGER: 727
 REAL: 880
 CHARACTER: 37
 Total CPUtime (sec): 3.80E-02

Table VI. Results of reactor simulations and comparison to experimental data.

Experiment #	061302	061902	072402	071102	062002	062602	062702	052202	070902	070302	072902	072502
Temperature (°C)	580	600	650	700	700	700	700	750	750	790	800	800
Pressure (atm)	1.18	1.18	1.17	1.17	1.18	1.18	1.18	1.16	1.18	1.15	1.10	1.16
Br ₂ /CH ₄ ratio	0.99	0.81	1.87	1.80	0.79	1.43	1.81	0.99	1.94	1.73	2.45	1.82
Nominal residence time (s)	27.0	17.3	4.9	4.8	15.4	19.9	16.2	22.2	4.5	4.2	13.5	14.5
% yield of HBr												
PLUG (no solid C)	49.7	49.9	48.4	48.4	51.5	49.5	48.5	59.7	48.0	50.0	56.8	53.7
PLUG (stick = 1)	80.4	77.4	98.7	99.6	89.6	97.7	99.7	99.3	100.0	99.8	100.0	100.0
CRESLAF (stick = 1)	51.1	51.3	52.5	58.0	61.4	68.6	68.0	82.7	69.1	80.4	99.8	92.2
Experiment	49.2	47.9	35.5	85.1	79.2	84.2	65.7	92.6	86.1	> 78.0	> 66.0	93.3
Equilibrium (no solid C)	98.5	99.2	79.7	82.9	99.7	99.5	82.3	99.8	76.8	86.4	74.9	82.5
Equilibrium (with solid C)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
% Br in bromocarbons												
PLUG (no solid C)	49.7	49.8	48.4	48.3	47.8	48.4	48.2	39.0	47.5	45.8	44.5	41.0
PLUG (stick = 1)	18.4	22.2	0.5	0.4	10.3	2.2	0.2	0.7	0.0	0.1	0.0	0.0
CRESLAF (stick = 1)	48.3	48.2	44.1	38.3	37.9	29.4	28.6	16.9	25.5	16.3	0.1	5.7
Equilibrium (no solid C)	1.5	0.8	0.8	0.4	0.3	0.4	0.4	0.2	0.2	0.1	0.1	0.1
Equilibrium (with solid C)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
% C deposited												
PLUG (stick = 1)	37.1	28.2	96.6	96.2	44.6	80.9	96.7	71.4	100.0	96.1	100.0	98.0
CRESLAF (stick = 1)	1.5	1.1	7.8	17.5	8.2	27.4	35.3	27.1	42.1	53.4	99.4	74.7
Equilibrium (with solid C)	97.3	96.9	100.0	100.0	99.0	99.8	100.0	99.6	100.0	100.0	100.0	100.0

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